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(TDM 69X04100)

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CONDITIONS OF SATURATED VAPOR PRESSURES
OF THE TWO COMPONENTS AND INERT
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Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

Attention: L. R. TOTH, TECHNICAL COGNIZANCE

CONTRACT 951581
Under NAS 7-100

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FLAMMABILITY OF OF_2 AND B_2H_6 UNDER THE CONDITIONS OF SATURATED VAPOR PRESSURES OF THE TWO COMPONENTS AND INERT PRESSURIZING GAS BETWEEN 200 AND 300°R

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ABSTRACT

The flammability limits of mixtures of B_2H_6 and OF_2 at their respective saturated vapor pressures between 200 and 300°R have been determined in the presence of the inert gases He and N_2 at total pressures of 100 and 500 psia. With one exception, B_2H_6 and OF_2 did not react explosively in the prescribed mixture ratios when held at the experimental temperatures. The one exception where an explosion occurred involved a mixture ratio such that the concentrations of OF_2 and of B_2H_6 were very nearly equal to the ratio of their respective vapor pressures at the experimental temperatures. Thus far there seems to be no rational explanation for the explosive behavior of this mixture in view of the fact that no such explosions occurred in similar and closely related mixtures.

Numerous explosions were observed when efforts to separate the reaction products were carried out by reducing the temperature to the extent that a liquid phase of OF_2 and a solid phase of B_2H_6 were present.

During determinations of whether the mixtures of B_2H_6 and OF_2 had reacted without explosion, B_2H_6 could be isolated from the mixture, and the absence of the expected reaction product BF_3 indicated that barring explosion no reaction had occurred.

FOREWORD

This work was carried out under Technical Direction Memorandum 69X04100, which prescribed the conditions under which the flammability limits of OF_2 and B_2H_6 were to be determined. The research was carried out by the Synthesis Research Group of Stanford Research Institute, M. E. Hill, Director; W. E. Tolberg, project leader; and R. S. Stringham, physical chemist. The Technical Cognizance for JPL was the responsibility of L. R. Toth.

I INTRODUCTION

The objective of the research under the TDM was to determine the flammability limits of mixtures of OF_2 and B_2H_6 under certain conditions. The temperature range was from 200 to 300°R or from approximately -162 to -107°C. The gaseous mixtures were prescribed to be those of the saturated vapors of each gas at the experimental temperatures combined with enough inert gas (N_2 or He) to build the pressure up to 100 or 500 psia.

The experimental apparatus was set up in such a way that a mixture of OF_2 and pressurizing gas was slowly released into a Monel metal sphere containing the prescribed quantity of B_2H_6 . The inlet of the reaction vessel was designed to assure mixing of the gases. The sphere was equipped with a thermocouple to detect exothermic reaction.

In a number of experiments, we attempted to observe whether OF_2 and B_2H_6 had reacted by separating the gases in the mixture. During these experiments, the apparatus was cooled to about 186°R. On cooling the mixture to this temperature, it invariably exploded often destroying the apparatus. Under these conditions, solid and vapor phases of B_2H_6 and liquid and vapor phases of OF_2 were present. Since these phases in contact always resulted in highly exothermic reactions, both explosive and nonexplosive, we concluded that cooling these mixtures to the extent that changes of phase occurred had to be avoided. These circumstances also described a flammability limit although outside the range of interest described in the TDM.

It should be noted that vapor pressures of OF_2 are unknown above about 233°R. Thus the pressures of OF_2 that were used were from a crude determination of the vapor pressure up to about 325°R. These data fell somewhat below the extrapolated curve, a not unexpected result.

In the following sections of this report we will discuss the results of this study and describe the experimental procedures used in obtaining them.

II DISCUSSION

The data obtained in these experiments are given in Tables I and II and plotted in Figures 1 to 4. Several explosions occurred during the experimental work and, as a result, all manipulations were carried out with caution. The experimental apparatus is shown in Figure 5. The mixtures of OF_2 and B_2H_6 with one exception failed to explode at reaction temperatures in the range from 200 to 325°R . When, as mentioned above, the mixtures were cooled to 186°R they exploded or reacted very exothermically. When, in one experiment, the temperature was raised to about 396°R , the mixture exploded. Thus we have observed explosions under three sets of conditions. In one, cooling below the freezing point of B_2H_6 results in explosions which, as will be shown later, are caused by the presence of condensed phases of both reagents. In the second, warming to about 396°R evidently exceeds the thermal activation required for reaction. In the third set of conditions, run No. 11 in Table I, we can offer no explanation for the explosion at reaction temperature.

In Figures 1 and 2, point No. 11 shows the B_2H_6 and OF_2 pressures, which within experimental uncertainty were equal to or less than the saturated vapor pressure curve. It is certain that the OF_2 was present only in the vapor phase. As outlined in the Experimental Section, the procedure ensured that OF_2 would always be present at a little less than saturated pressure. However, a small amount of B_2H_6 in liquid phase could have been present at any or all of the points studied, due mainly to the uncertainty in temperature during addition. Regulation of temperature was good to $\pm 2^\circ\text{C}$ or $\pm 3.6^\circ\text{R}$. During any given experimental run, this variation could yield a liquid phase of B_2H_6 . However, because no explosions occurred during many similar runs, the presence of a liquid phase of B_2H_6 cannot be the explanation for the occurrence of an explosion during run No. 11. Thus we can offer no explanation for this event.

Table I

Run	Temp (°R)	Total Press (psia)	Press He (psia)	Press OF ₂ (psia)	Press B ₂ H ₆ (psia)	$\frac{\text{OF}_2}{\text{B}_2\text{H}_6}$	Explosion At R _x Temperature	Remarks
1	234	103	86	1.7	0.29	58.5	No	
2	278	495	411	81	3.3	24.6	No	
3	238	497	477	20	0.35	57.0	No	
4	302	485	313	165	6.8	24.2	No	
5	294	101	0	94	4.7	20.0	No	
7	292	105	0	100	4.5	22.2	No	Small expl on cooling
8	299	128	0	121	6.6	18.4	No	
9	292	97	0	91	4.5	20.2	No	Destructive expl on cooling
10	280	88	0	84	3.9	21.6	No	No cooling
11	288	101	0	96	4.9	19.6	Yes	Expl after 2 min Destructive expl
12	295	103	19	82	2.4	34.2	No	Destructive expl on cooling
13	250	490	454	35	0.77	58.4	No	Destructive expl on warming to 396°R
14	214	108	100	7.4	0.10	74.0	No	
15	214	495	487	7.4	0.10	74.0	No	
16	240	104	83	20.6	0.43	48.0	No	
17	262	101	48	52	1.36	38.2	No	
18	324	490	232	258	14.2	18.2	No	
19	324	265	0	251	14.2	17.7	No	
20	200	100	97	2.7	0.03	90.0	No	
21	200	485	482	2.7	0.03	90.0	No	

Data for the flammability of saturated OF₂ and B₂H₆ vapors between 325 and 200°R with the inert gas He added for studies between 100 and 500 pounds total pressure.

Table II

Run	Temp (°R)	Total Press (psia)	Press N ₂ (psia)	Press OF ₂ (psia)	Press B ₂ H ₆ (psia)	$\frac{\text{OF}_2}{\text{B}_2\text{H}_6}$	Explosion At R _x Temperature	Remarks
I	266	475	425	49	1.65	29.6	No	
II	262	106	57	47	1.6	29.4	No	
III	304	478	360	112	6.0	18.7	No	
IV	325	470	220	246	14.2	17.4	No	
V	214	102	94	6.2	0.10	62.0	No	
VI	240	105	85	20	0.40	50.0	No	
VII	240	475	455	20	0.40	50.0	No	
VIII	324	265	0	251	14.2	17.7	No	
IX	292	105	0	100	4.5	22.2	No	
X	200	100	97	2.7	0.03	90.0	No	

Data for the flammability of saturated OF₂ and B₂H₆ vapors between 325 and 200°R with the inert gas N₂ added for studies between 100 and 500 pounds total pressure.

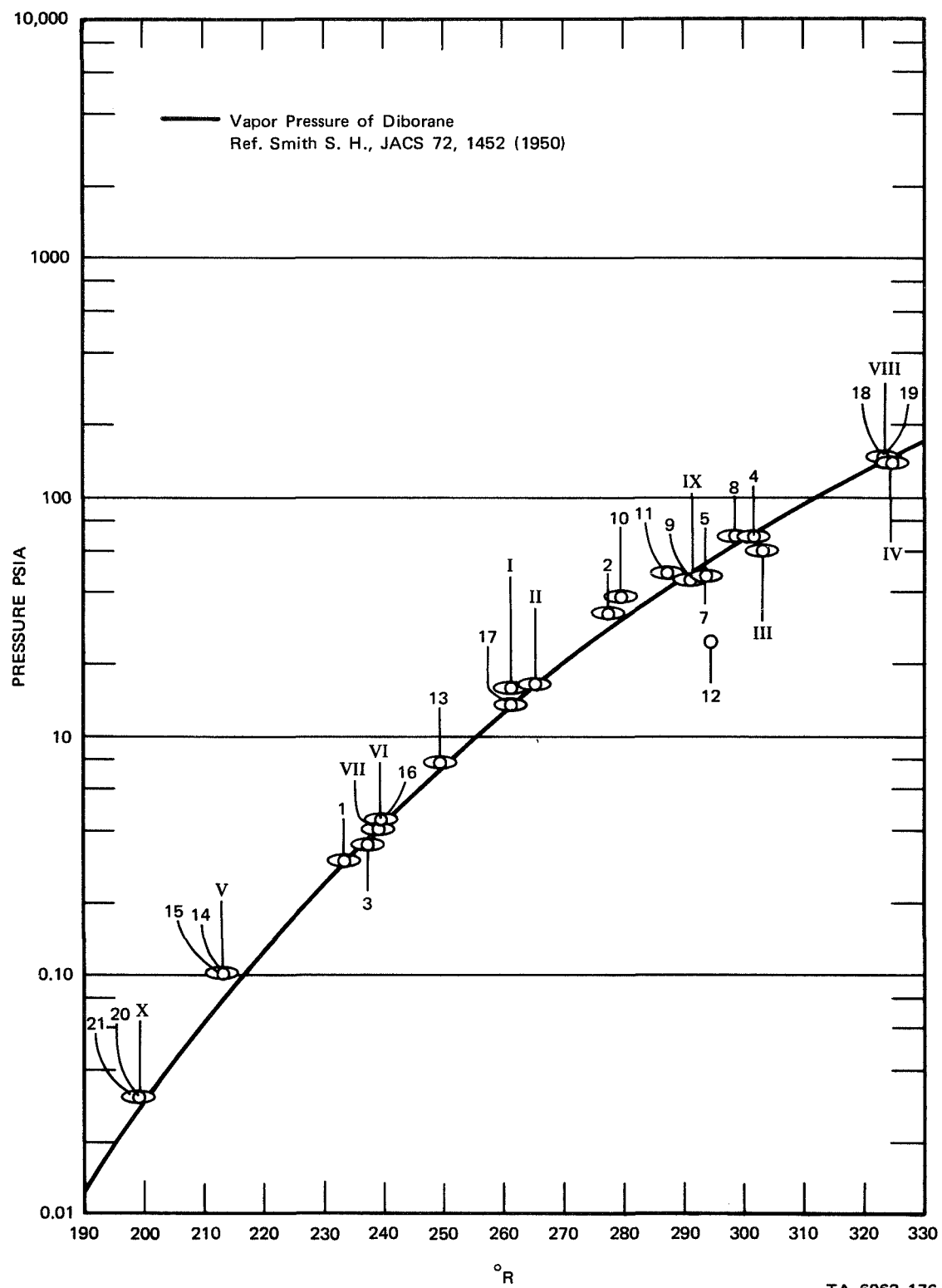


FIGURE 1 PRESSURE OF DIBORANE IN REACTION VESSEL

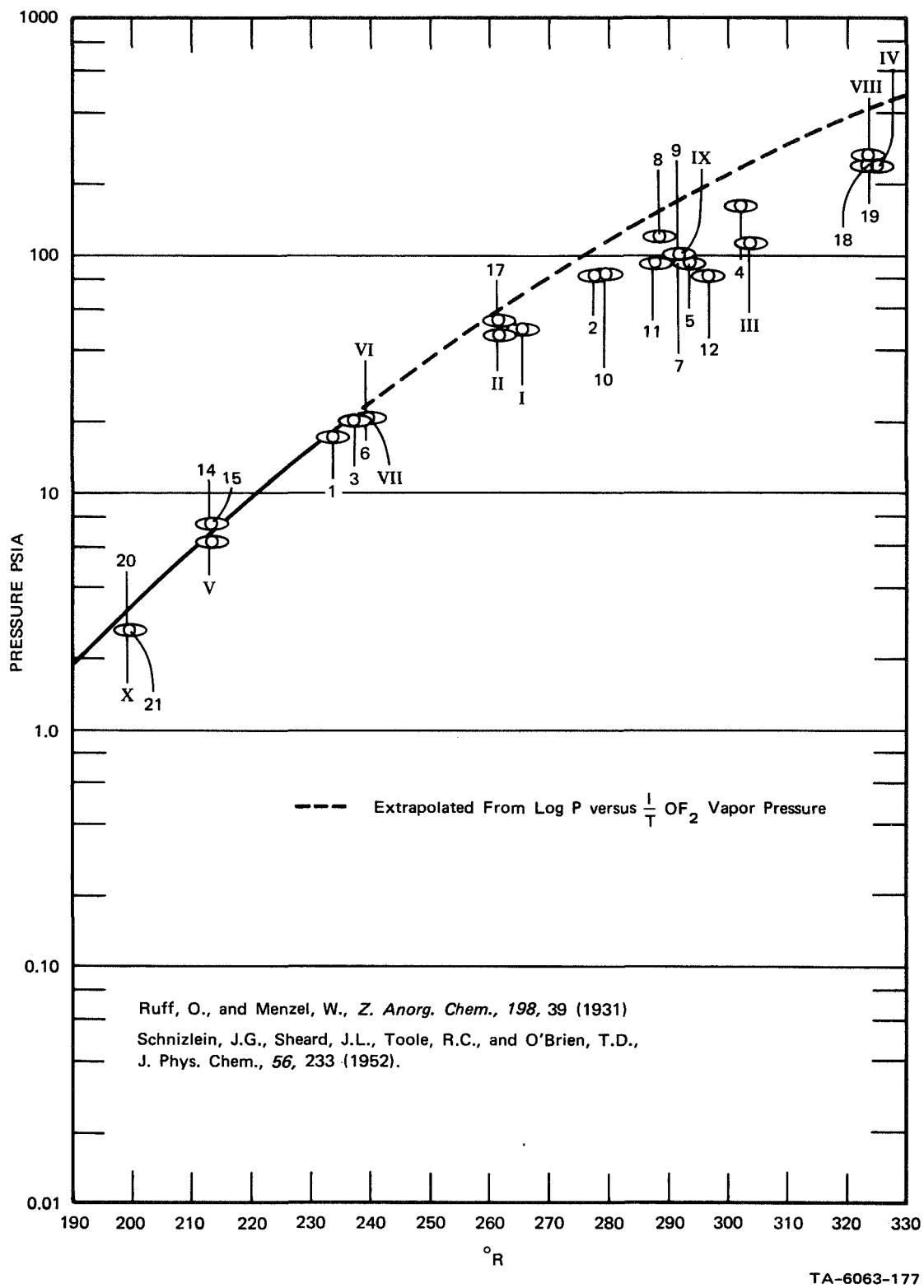
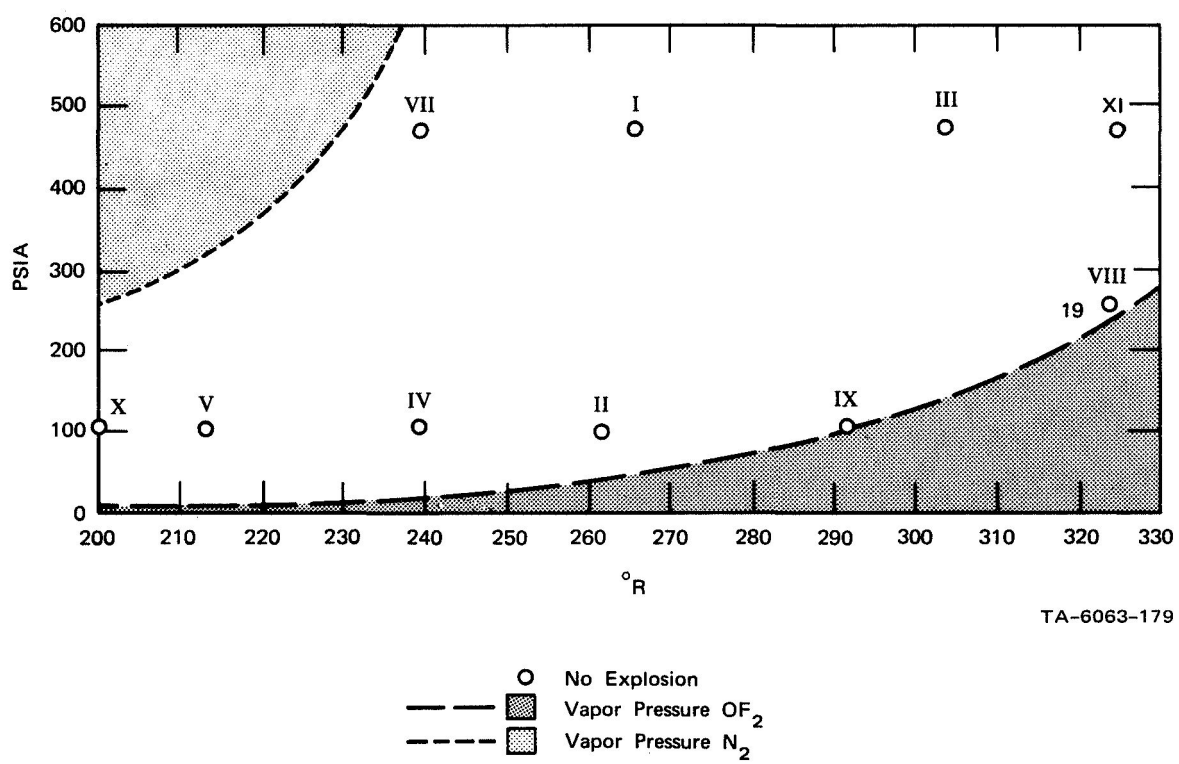
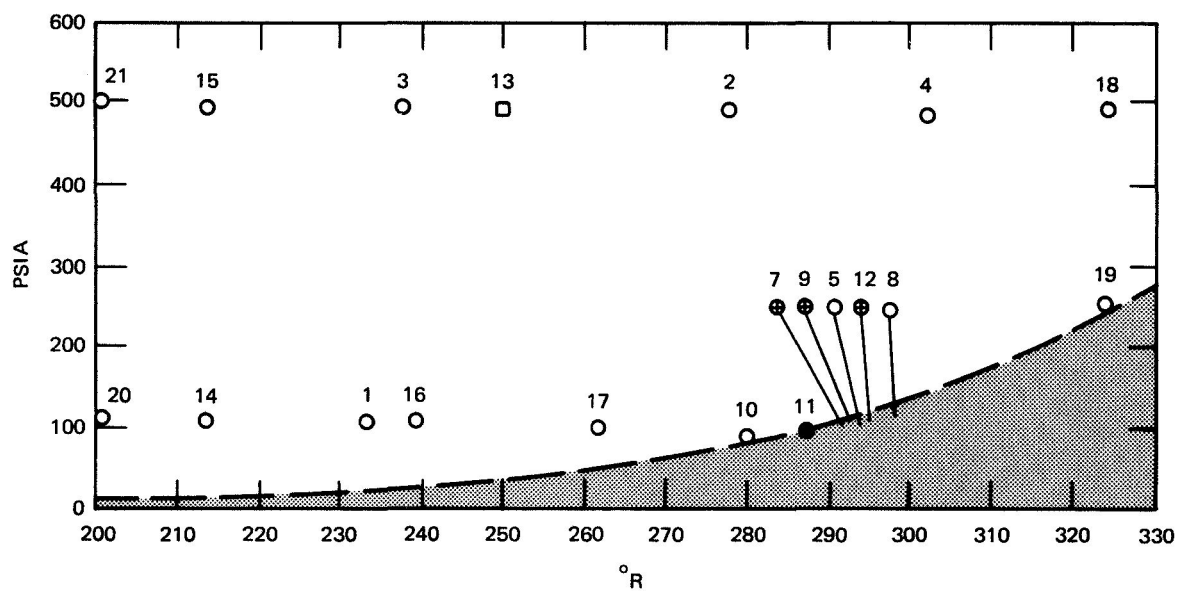


FIGURE 2 PRESSURE OF OXYGENDIFLUORIDE IN REACTION SPHERE



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FIGURE 3 $\text{OF}_2/\text{B}_2\text{H}_6/\text{N}_2$ SYSTEM



- No Explosion
- ⊕ Explosion After Cooling
- Explosion After Warming
- Explosion at Reaction Temperature
- Vapor Pressure of OF_2

FIGURE 4 $\text{OF}_2/\text{B}_2\text{H}_6/\text{He}$ SYSTEM

On cooling the mixtures to 186°R, both OF₂ and B₂H₆ condense; B₂H₆ also freezes (-165.5°C, 193.2°R) and the resulting mixture of phases reacts either of two ways. We have observed relatively slow reactions which are exothermic, and we have also observed very fast reactions which are explosive and also, of course, exothermic. These experiments involving cooling of the mixture were carried out to determine the extent of a possible very slow reaction between OF₂ and B₂H₆. It was desired to separate residual B₂H₆ or its OF₂ reaction products from the large excess of OF₂. Reaction is expected to form B, BF₃, H₂, and H₂O.¹ We expected some difficulty in detecting small amounts of BF₃ because it can be lost in two ways. In fluorine-passivated metal systems, metal fluorides on the walls can absorb BF₃ probably to form BF₄⁻ salts. In addition, BF₃ and water form complexes.

The technique for isolating the expected higher boiling products of reaction was developed slowly through the first 18 experiments. We first used the assumption that B₂H₆ in a large excess of OF₂ might react slowly throughout the experiment giving off heat insufficiently fast to affect the thermocouple. Thus we sought to isolate BF₃ at its freezing point, about 262°R. In several experiments, the gases were cooled to about 200°R and no explosions occurred. The OF₂ was removed by venting followed by pumping. The collector was subsequently warmed to release any residual gases frozen out at 200°R and ir spectra were taken and analyzed. Only the normal impurities of OF₂ were found: SiF₄, SF₆, CO₂, SO₂F₂, and possibly HF. This procedure also resulted in removal of B₂H₆ which we later showed to be present in the mixture. No unequivocal evidence for BF₃ was found.

After cooling the mixtures only to temperatures above the freezing point of B₂H₆, we attempted cooling to lower temperatures. When the mixtures were cooled below the freezing point of B₂H₆, explosions invariably occurred. These were violent explosions which damaged the apparatus and destroyed the 2-in. diameter Monel metal sphere containing the reactants.

¹R. A. Rhein, NASA Space Summary, 37-42, Vol. IV, 1966, p. 73.

In order to determine whether B_2H_6 was present in the mixture, we then, in run No. 18, vented the mixture held at the reaction temperature until the pressure was one atmosphere. At this time, the apparatus was cooled to below the freezing point of B_2H_6 and the remaining OF_2 was pumped away. No explosion occurred under these conditions. Infrared spectra of the gas retained in the system showed that only B_2H_6 was present.

None of the impurities known to be present in OF_2 was detected. Thus this method of isolation retains only the major concentrations of condensables and no small amounts of reaction products would have been detected. It is concluded therefore that B_2H_6 can exist in OF_2 but the extent to which it reacts, if at all, is not known. However, it seems reasonable that no reaction occurs unless it is an explosive one.

In summary, mixtures of OF_2 and B_2H_6 at very near their respective saturated vapor pressures in the temperature range from 200 to 325°R and pressurized to 100 or 500 psia with either He or N_2 are with one exception not flammable. There is no immediately obvious explanation for the exception.

III EXPERIMENTAL SECTION

Apparatus

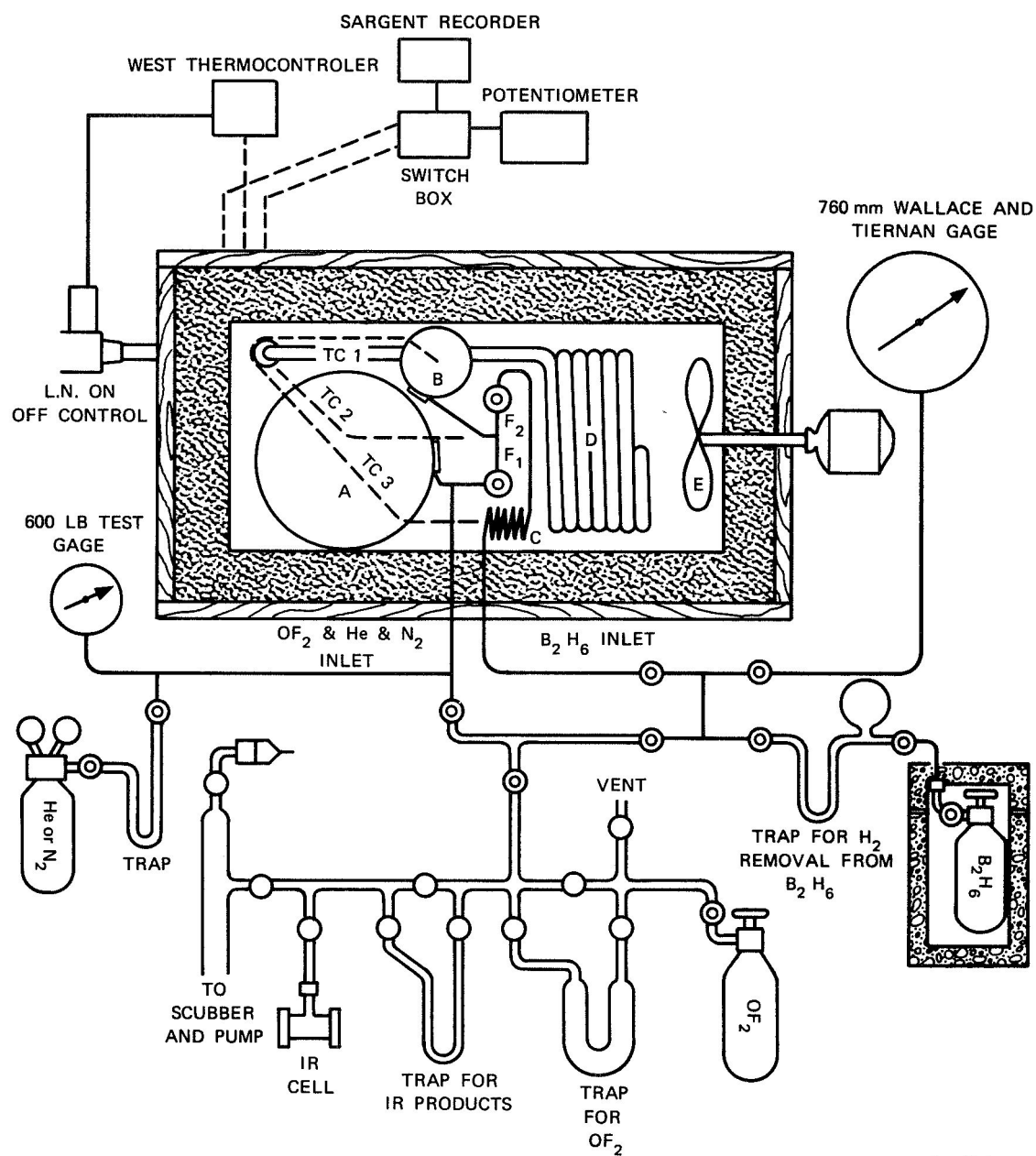
The apparatus used for this study is illustrated in Figure 5. The low temperature portion of the system was contained in a wooden box lined with 2-in. slabs of styrofoam. The two valves F_1 and F_2 were operated by an extension wrench through two holes drilled in the box. Other holes for pipes, thermocouple leads, and the fan motor shaft were drilled as needed.

The reaction system consisted primarily of two spheres A and B and connecting lines and valves within the insulated box. Sphere A was used to meter OF_2 and to mix pressurizing gas. Sphere B was the mixing chamber for OF_2 , pressurizing gas, and diborane. Coil C was used to present a high surface-to-volume vessel for the trapping of condensable gases.

Temperature regulation was achieved with a West thermocontroller which used thermocouple 2 (TC-2) as a sensor and through a solenoid valve admitted cold N_2 gas into coil D. The cold N_2 flowed into the box from coil D near fan E, which then circulated the cold N_2 throughout the box. Thermocouples in vessel B (TC-1) and at coil C (TC-3) indicated that the controller was maintaining temperatures to within $\pm 2^\circ C$, as specified for the controller.

The remainder of the apparatus illustrated is conventional Monel metal vacuum line suited for use with OF_2 and B_2H_6 . Most joints were Heliarc welded but some were silver soldered with 72/28 Ag/Cu alloy. The entrance pipe to the reaction sphere was soldered in place so that the gases would enter on a tangential path. This path was selected to assure the best mixing of gases. The same design was used for sphere A to mix pressurant gas with OF_2 .

The volume of sphere A was very nearly 1.14 liters and that of sphere B was 68.6 cc. As will be outlined in the paragraphs on procedure,



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- Dry Ice Storage Box for B_2H_6
- Styrofoam Insulation for Cold Temperature Bath
- Wood Box for Bath
- Hoke Values with Teflon Gaskets
- Hoke Values with Copper Bellows
- 1/8" Copper Tubing
- 1/4" Copper or Monel Tubing

FIGURE 5 EXPERIMENTAL SYSTEM

the relative size of the volumes determined total pressure required in sphere A to obtain the correct pressures in sphere B.

Procedure

The B_2H_6 (Thiokol) supply was maintained at dry ice temperature throughout the experimental work in order to minimize decomposition into H_2 and other boron hydrides. As shown in Figure 5, a U-tube trap, which could be cooled with liquid N_2 , was used for the removal of any hydrogen present in the B_2H_6 . After purification, the B_2H_6 was admitted to sphere B until it reached the literature value for the vapor pressure of B_2H_6 at the temperature of the cold bath as measured on TC-1. These vapor pressures were low enough to measure with a Wallace and Tiernan 0-760 mm gage, Model FA-145.

As noted before, vapor pressures of OF_2 above about $233^\circ R$ are not available in the literature and had to be established in this work between 233 and $325^\circ R$. The OF_2 was obtained from two sources: Allied Chemical and Ozark Mahoning. The purification method used was to pump on the liquid OF_2 at liquid nitrogen temperature mainly to remove most of the nitrogen and at least some of the oxygen that might be present. All other impurities would remain in the OF_2 but would contribute little if any to the vapor pressures being observed. The gage used for OF_2 was a 600-psia test gage by Ashcroft. This was deemed adequate to read pressures up to about 250 psia of OF_2 and the combined pressure of OF_2 and pressurant gas in excess of 500 psia.

The trap for OF_2 shown in Figure 5 was used as an accumulator to build up pressures of OF_2 as needed; viz., when the tank pressure of OF_2 fell below the pressure needed in the metering vessel.

The vapor pressure of OF_2 was established in the following manner: OF_2 was added to sphere A in increments until the addition of the last increment failed to increase the pressure. As noted in Figure 2, there is some scatter among the points, which may be attributed both to the range in the temperature control and to the pressure test gage used,

especially in the region of higher pressures of OF_2 . It appears from the points included in the region where vapor pressures are not known that a reasonably smooth curve could be drawn leaving a number of points somewhat below the probable true saturation pressure. Nevertheless, the results from these points are considered valid and reasonable in view of the large excess of OF_2 relative to B_2H_6 .

The ratio of the volume of sphere B to the combined volume of the metering vessel (sphere A) plus sphere B is about 0.057. Thus the amount of OF_2 present in the metering volume, sphere A, cannot exceed the amount needed to form a saturated vapor pressure of OF_2 in the combined volumes. If the amount of OF_2 exceeded this value, a liquid phase of OF_2 would have been present in the reaction vessel. To avoid this we attempted to make the final pressure of OF_2 in the system equal to or slightly less than saturated. As will be noted from Figure 2, some points were measurably below saturation.

The last increment of OF_2 added to the metering volume could be estimated from PV measurements in the lines external to the cold bath and we attempted to make the last increment less than 5.7% of the OF_2 present so that on expansion into the combined volumes, no liquid phase would result. This assumes, of course, that none of the second to last increment of added OF_2 condensed and the technique used to detect this was the constancy of pressure increase relative to the amount added. In this, the perfect gas law was assumed to be valid for evaluating differences. It is clear from the number of points below the curve that pressure and temperature measurements were not sensitive enough to perform these observations with more than adequate precision.

In each experiment, when the proper pressure of OF_2 had been obtained, pressurant gas was added to the metering vessel such that the total pressure on expansion into the reaction vessel would be either near 100 or 500 psia. Tables I and II show the values observed. At temperatures above about 287°R , the pressure of OF_2 exceeded 100 psia and no pressurant gas was added as shown in Figures 3 and 4. When the metering vessel was filled with the required gases, the mixture was first allowed

to stand for about 20 min to assure mixing. Then the mixture was added to the sphere B containing the B_2H_6 . The addition process was carried out relatively slowly requiring 3 to 5 min to complete. The OF_2/B_2H_6 /pressurant gas mixtures were then allowed to stand for 20 to 30 min or until explosion occurred (run No. 11).

The conditions under which explosions did occur and the procedures for isolating reactants or products were described in the Discussion Section.

The explosions that occurred were very violent, rupturing the reaction vessel, sphere B, and connecting tubes. In addition the cold bath box itself was all but demolished. The experiments were carried out in a hood with plexiglas shields, and no fragments penetrated the shields. One explosion occurred when OF_2 itself was condensed in a trap. The trap was made of Kel-F which on examination of fragments appeared not to have reacted with the OF_2 . We could only speculate that the trap contained an impurity with which the OF_2 reacted. This explosion occurred during the first experiment and we therefore conducted all subsequent experiments with a great deal of caution.